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CHEMICAL TRANSFORMATIONS IN ACID RAIN

Volume I. New Methodologies for Sampling and Analysis of Gas-Phase Peroxide

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New methodologies for the sampling and analysis of gas-phase peroxides (H_2O_2 and organic peroxides) using (a) diffusion denuder tubes and (b) gas-to-liquid transfer with prior removal of ozone have been investigated. The purpose was to develop an interference-free method for determining H_2O_2 in ambient air. A denuder approach using ferrous (1,10-phenantholine)-coated tubes was unsuccessful; although H_2O_2 was removed in the approach, the capacity was low and ozone was also removed, possibly through surface decomposition to H_2O_2 and its radical precursors. Gaseous peroxide in compressed air streams could be collected in impingers without artifact formation from surface ozone decomposition if O_3 was first removed by gas-phase titration with nitric oxide.

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ABSTRACT

New methodologies for sampling and analysis of gas-phase peroxides (H_2O_2 and organic peroxides) using (a) diffusion denuder tubes and (b) gas-to-liquid transfer with prior removal of ozone have been investigated. The purpose was the development of a interference-free method for determining $H_2O_2(g)$ in ambient air. A denuder approach using ferrous-(1,10-phenantholine) coated tubes was unsuccessful for, although H_2O_2 was removed, the capacity was low and ozone was also removed, possibly through surface decomposition to H_2O_2 and its radical precursors. Gaseous peroxide in compressed air streams could be collected in impingers without artifact formation from surface ozone decomposition if O_3 was first removed by gas-phase titration with nitric oxide.

CONTENTS

ABSTRACT..... iii

TABLES..... vi

FIGURES..... vii

ACKNOWLEDGMENT..... viii

INTRODUCTION..... 1

EXPERIMENTAL..... 5
Reagents..... 5
Apparatus..... 6
Procedures..... 9
Calibrations and Quality Assurance Activities..... 11

RESULTS AND DISCUSSION..... 13
Aqueous Determination of H_2O_2..... 13
Denuder Tube Sampling..... 14
Gas-to-Liquid Sampling after O_3 Removal..... 17

SUMMARY AND CONCLUSIONS..... 21

REFERENCES..... 23

TABLES

NUMBER		PAGE
1	Depletion of Ferroin-Coated Denuders.....	15
2	Collection of H_2O_2 from Ozone-Containing and Ozone-Free Air Streams.....	18

FIGURES

NUMBER		PAGE
1	Apparatus for H_2O_2 Generation and Impinger Collection.....	7
2	Modified Apparatus for H_2O_2 Generation and Impinger Collection.....	8
3	Flow Schematic of POHPAA Fluorescence Analysis System for Aqueous H_2O_2: A = TRIS Buffer (pH=8.5); B = HRPO and POHPAA in TRIS buffer; C = EDTA in TRIS buffer; D = catalase in TRIS buffer; E = waste; = mixing coils; 0 = degassers.....	12

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INTRODUCTION

The purpose of this research task was to develop fundamentally new methods for sampling and analysis of gas-phase hydrogen peroxide ($H_2O_2(g)$) and organic peroxides if possible, in air through the use of diffusion-denuder tubes. In addition, sampling methods for H_2O_2 using gas-to-liquid transfer and capable of avoiding *in situ* production of H_2O_2 from ozone (O_3) decomposition and other processes were studied. The goal of the research was an interference-free method for gas-phase peroxides with 0.1 ppb limit of detection and 15 min time resolution.

Much analytical effort has been expended in the past few years in measuring gaseous and aqueous H_2O_2 following the recognition that H_2O_2 could oxidize dissolved S(IV) rapidly throughout the pH range of rain, cloud and fog waters (pH 2-7) (Penkett et al., 1979). Furthermore, the high solubility of H_2O_2 in water led to significant (1-100 μM) Henry's law equilibrium concentrations in cloudwater even at low ppbv gaseous H_2O_2 levels in clear air entering clouds. Methods for determining liquid-phase H_2O_2 have been developed using several approaches: luminol chemiluminescence (Kok et al., 1978); POHPAA fluorescence (Guilbault et al., 1968; Kunen et al., 1983; Lazrus et al., 1983); scopoletin fluorescence quenching (Zika and Saltzman 1982); and peroxyoxalate chemiluminescence (Klockow and Jacob, 1983). Attempts to measure gas-phase hydrogen peroxide by collection in impingers or by other dissolution techniques have been shown to be generally unreliable (Heikes et al., 1982; Zika et al., 1982; ten Brink et al., 1983) due to the *in situ* formation of hydrogen peroxide from low-solubility constituents of ambient and/or compressed air during collection by impingers. Recently reported observations (Heikes, 1984) are interpreted to indicate that surface-initiated ozone decomposition

via HO_2^- and O_2^- intermediates is the likely mechanism of "artifact" H_2O_2 formation (see also Stahelin and Hoigne, 1982).

The research approaches suggested at the initiation of this project for artifact-free sampling of $H_2O_2(g)$ included:

A. selective, reactive sampling onto a coated denuder tube, employing H_2O_2 redox chemistry;

B. suppression of *in situ* H_2O_2 formation in gas-to-liquid sampling devices using radical scavengers;

C. suppression of *in situ* H_2O_2 formation by selective removal of ozone;

D. selective passive sampling of H_2O_2 (after O_3 removal) onto a solid sorbent or denuder tube, or passive collection onto a condensation surface;

E. investigation of immobilized peroxidase-flow injection analysis (FIA) systems for H_2O_2;

F. use of counter-flow, selectively permeable-membrane, continuous-analysis systems for H_2O_2.

Nearly all of the work performed for the research task related to approaches A and C. Radical scavengers (approach B) were considered for elimination of *in situ* production of H_2O_2 in gas-to-liquid samplers. This approach has been used to interrupt chain reactions in solution; for example, n-octane was used to interrupt the chain decomposition of O_3 + hydrazine (Tuazon et al., 1983). However, this technique is only successful if the route of $R^{\cdot}(aq)$ to H_2O_2 (aq) product in solution ($R^{\cdot}$ = hydrocarbon radical) is the only significant one for H_2O_2 formation. Since it appears (Heikes, 1984) that non-radical surface decomposition of O_3 to HO_2^- is the key step in the artifact production of H_2O_2, addition of a radical scavenger would at best eliminate only a portion of the artifact H_2O_2.

Two approaches to selective passive sampling (approach D) have been attempted by ten Brink et al. (1983). Experiments contacting aluminum, copper, iron and silver sheets or gauze with ozone-containing air (100 ppb to 5 ppm O_3) indicated that only aluminum (Al) removed O_3 at high efficiency. The reactivity of the surface degraded after an hour or so and had to be regenerated by cleaning with dilute mineral acids for each experiment. Experiments conducted with generated $H_2O_2(g)$ (10 ppb - 10 ppm) contacting an Al-lined glass impinger indicated that the transmission efficiency of the Al "ozone trap" was about 25% for H_2O_2. Further experiments using parallel sampling trains sampling ambient air containing 100-200 ppbv O_3 resulted in the collection of much more H_2O_2 in the Al-lined impinger than in the control glass impinger.

The conclusions one may draw from the experiences of ten Brink et al. (1983) are that Al surfaces collect ozone quantitatively at the start but have low capacity. The transmission of H_2O_2 through Al-lined impingers is reproducible but low (~25%). Ozone is decomposed to form gaseous H_2O_2 on Al surfaces and hence pre-sorption of O_3 on Al surfaces is not a viable means of eliminating artifact H_2O_2 in the gas-to-liquid collection of H_2O_2 from ambient air.

No work was done on approach E (the use of immobilized peroxidase enzyme systems) since it does not appear to solve the problem of artifact H_2O_2 formation during sampling. It does appear to have some real advantages in designing semi-continuous liquid-phase H_2O_2 analysis systems in that POHPAA reaction time can be controlled and thus the analytical reaction can be turned on and then off at precise intervals during sample processing.

The use of counter-flow, selectively-permeable membrane, continuous-analysis systems (approach F) for other soluble gases has been reported by Dasgupta (1984). Both hydrophillic membranes with system response times of a few minutes and hydrophobic membranes (porous PTFE) with response times of a few seconds have been reported. No work has been done in this project to evaluate these devices, but it is an extremely promising approach which, combined with approach (C) for selective ozone removal, should form the basis for future research in gaseous H_2O_2 sampling and analysis.

EXPERIMENTAL

Experiments in this task were conducted using a system in which gas-phase hydrogen peroxide was reproducibly generated in the 1-500 ppbv range by multiple dilutions with compressed air, with facilities to subsequently humidify the air and add ozone and nitric oxide to the diluted air stream. Parallel air streams were then formed with appropriate mixing chambers, and peroxide was collected in parallel series of 2 or 3 midget impingers which were followed by flow meters, charcoal traps for ozone and H_2O_2, and a common, selectable inlet line to the ozone analyzer. Denuder tubes were tested in this setup by placing them in the air streams after, or in place of the mixing chambers.

Reagents

Ozone was generated using an AID, Inc. ozone generator containing a UV light source. Nitric oxide was added to the air stream (tank breathing air) from a certified tank source of 208 ppm NO in nitrogen (Scott Environmental Technology). Hydrogen peroxide in air was generated from diluted solutions of reagent grade, 30% aqueous H_2O_2. Analysis of aqueous H_2O_2 was conducted by the peroxidase-catalyzed p-hydroxyphenylacetic acid (POHPAA) fluorescence technique employing separately added or premixed solutions of 1.6 mM POHPAA (Eastman), 5 μM horseradish peroxidase (Sigma Chem. Co.), ~1 mM Na_4EDTA, and 0.175 M TRIS (tris-[hydroxy-methyl]-aminomethane) buffer (Sigma Chem. Co.) adjusted to pH 8.5 with concentrated HCl. Selective removal of H_2O_2 was accomplished by addition of catalase enzyme (~0.01 mg/mL, Sigma Chem. Co.).

Apparatus

The apparatus used for the experiments as originally constructed is shown in Figure 1. Compressed breathing air was split into four streams. Stream one (top stream in Fig. 1) (10-50 cc. min^{-1}) was passed over diluted H_2O_2 contained in a glass vessel immersed in a thermostatted bath, through a metal (later Teflon) restrictor for flow control and diluted with 50-150 cc. min^{-1} of air in a second stream. Final dilution was obtained with a third stream (350-1850 cc. min^{-1}) in a second dilution step. For experiments with added ozone part of the second dilution air (~400 cc. min^{-1}) was passed through the AID Ozone generator and added to the stream without any cleanup steps. The valve prior to the H_2O_2 solution is an on/off valve whereas the dilution air streams contained a needle valve to regulate the flow. In this way the $H_2O_2(g)$ generator (H_2O_2 solution with thermostatted capillary) could be pressurized and the restrictor maintained as a critical orifice, whereas the dilution air streams were at near-atmospheric pressure. The temperature and concentration of the H_2O_2 solution could then be varied to provide a range of gas-phase concentrations.

The mixing chambers were 2L-Erlenmeyer flasks and all tubing and connectors up to the impingers were constructed of Teflon. Impingers were standard 50 mL midget impingers containing 25 mL of Millirho purified water (>10 MΩ, Millipore Corp.) Flow meters were standard Matheson or Lab-Crest models, calibrated using a wet test meter. The ozone analyzer was a Monitor Labs Model 8410 ethylene-chemiluminescence analyzer. Excess exhaust gas was vented through charcoal traps into the laboratory.

Later experiments were performed using the slightly modified apparatus in Figure 2. Changes permitted humidification of a portion of the dilution

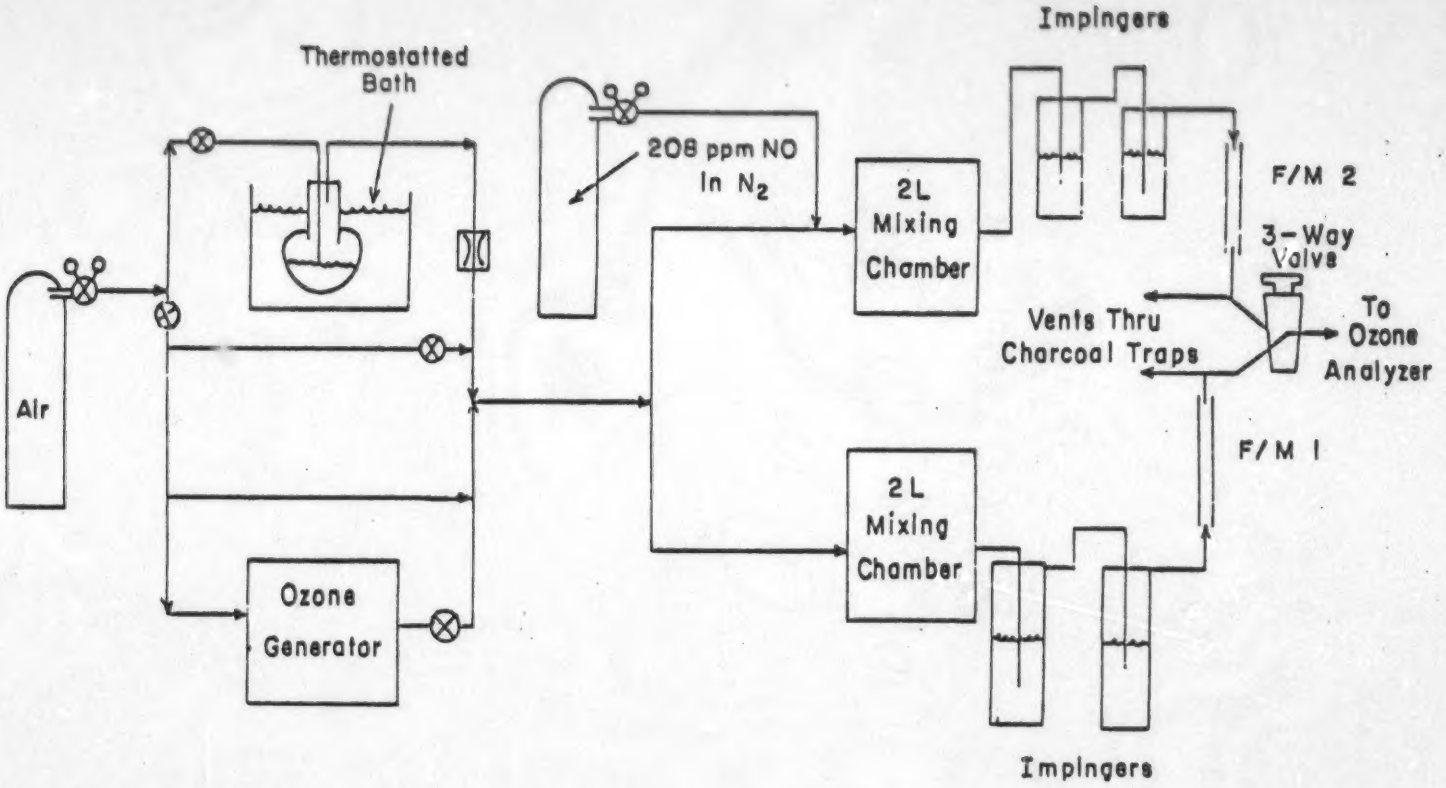

FIGURE 1

APPARATUS FOR H_2O_2 GENERATION AND IMPINGER COLLECTION

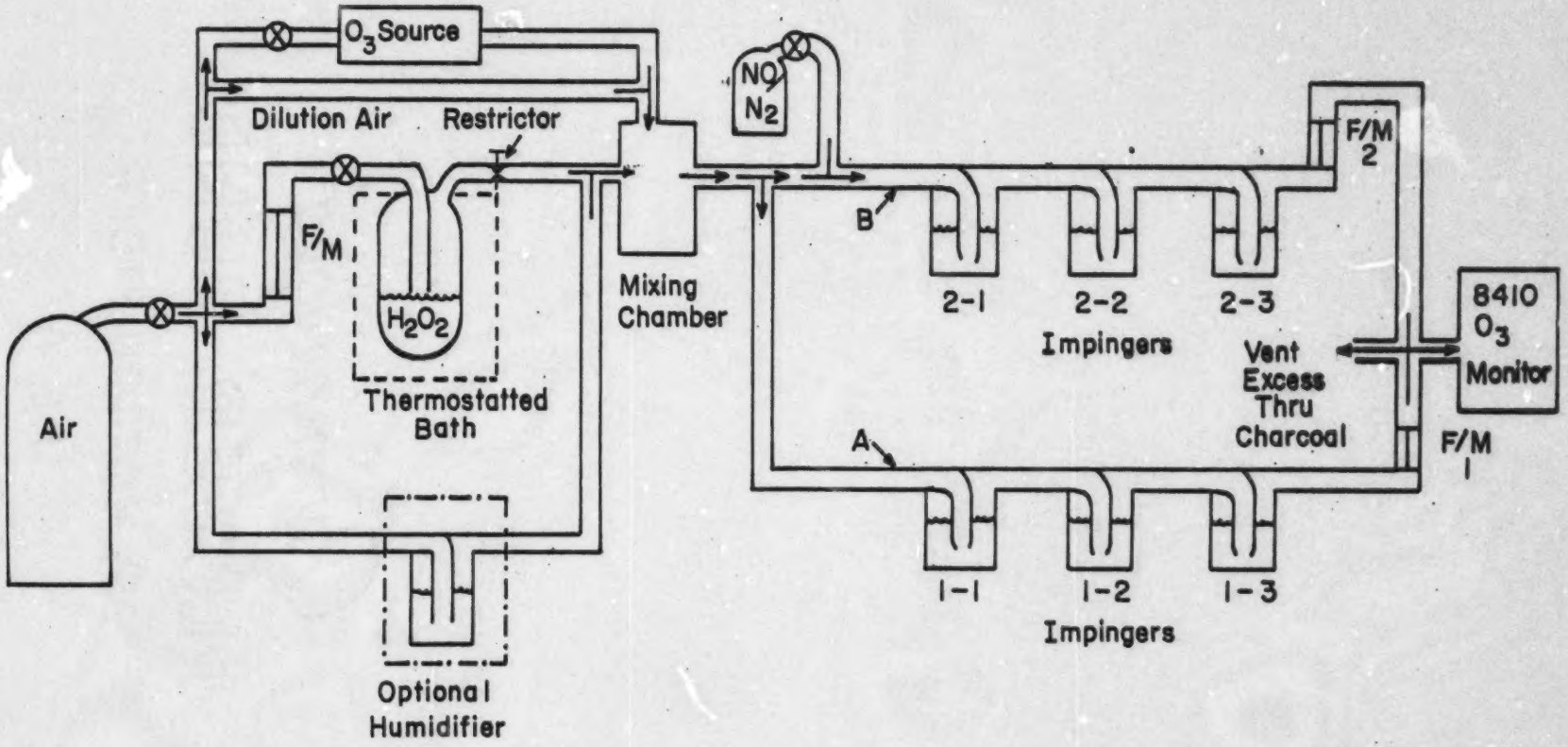

FIGURE 2

MODIFIED APPARATUS FOR H_2O_2 GENERATION AND IMPINGER COLLECTION

air, better temperature control (10-15°C) of the liquid H_2O_2 solution reservoir. Three impingers were used in series to collect the $H_2O_2(g)$ samples. In addition, because of observed losses of H_2O_2 even in the 100-200 ppbv concentration range, the 2L glass mixing chambers were removed and replaced by a single 1L polyethylene bottle placed prior to stream division. No mixing chamber was provided after NO addition to stream 2 in order to minimize $H_2O_2(g)$ losses.

Diffusion denuder tubes containing coatings of Fe(II)-1,10-phenanthroline were tested in experiments by placing them in the flow streams after division at points A and B, just prior to impingers 1-1 and 2-1, respectively.

Aqueous H_2O_2 in each of the six impingers was analyzed after each experiment using the POHPAA fluorescence method by sample injection into a flow injection system that included a multi-channel peristatic pump (Technicon) and a Farrand Model R2 flow-through fluorimeter. The variations in procedures using this system are detailed below.

Procedures

Experiments were conducted using the apparatus in Figures 1 or 2 by generating various gas compositions: compressed air, ~6 ppm NO in air, 10-300 ppbv H_2O_2 in air, 100-400 ppbv O_3 in air and various combinations of H_2O_2, O_3 and NO in air. The generated gas streams were scrubbed by bubbling through 2 or 3 bubbler solutions sequentially, with the gas streams analyzed for residual O_3 and the liquid bubbler contents for collected $H_2O_2(g)$ and any aqueous H_2O_2 formed during sample collection.

The coating reagent for the diffusion denuder tubes was prepared by evaporating to dryness the reagent grade 0.01 M Fe(1,10-phenanthroline)

solution, reconstituting it in methanol at about the same concentration, pouring a portion of it down the tube and drying it under rotation with a stream of N_2. Tubes were sealed and stored in the dark until use.

The dual fluorimeter system for determination of aqueous H_2O_2 by the POHPAA-fluorescence technique has been described in informal reports (Schwartz et al, 1984) and is an improved version of the single fluorimeter apparatus used by Kelly et al. (1984). The sample's total peroxide content was measured in one flow line. A second flow line measured residual fluorescence after selective destruction of H_2O_2 with catalase. Successive additions of $\sim 10^{-3}$ M EDTA, catalase or water (right or left streams, respectively) and the reagent (1.6×10^{-3} M POHPAA + 5×10^{-6} M horseradish peroxidase in pH 8.5 TRIS buffer) were mixed together in a system designed to minimize sample consumption for cloud water analysis. Single channel operation was possible when catalase addition was not required. The carrier stream for the sample stream in both channels was water.

The system as described above was found to have significantly poorer limits of detection (LOD) compared to that reported by Kelly et al. (1984) and by Lazrus et al. (1983); usually the LOD for H_2O_2 was ~3 ppb aqueous (~0.1 μM). The problem was traced to mixing noise brought about by the fact that, although the carrier was water and the catalase and EDTA solutions were made up in water, the reagent was necessarily made up in TRIS buffer. Channeling and other effects apparently led to inhomogenously distributed POHPAA dimer concentrations and hence fluorescence intensity fluctuations in the measurement cell. Preparing the EDTA and catalase (or diluent) solutions in pH 8.5 TRIS buffer was not adequate to reduce the noise. Recently it has been established (cf. Figure 3) that injection of the sample into a

TRIS buffer carrier solution and addition of a degasser unit just prior to the fluorimeter flow cell are required to reduce the mixing noise and achieve a limit of detection of ~0.3 ppb (~0.01 μM). The degasser's critical function is to provide a mixing volume (1-2 mL) adequate to ensure POHPAA concentration homogeneity but insufficient to significantly broaden the fluorescence response peak.

The modified fluorescence-FIA system with 0.3 ppb LOD was not available for most of the experiments conducted in this task, hence an alternate, "stopped-flow" approach to aqueous H_2O_2 analysis was developed which was manually operated but able to attain the desired sensitivity. In this approach, 3 volumes of sample were mixed, with one volume of peroxidase/POHPAA/EDTA solution in pH 8.5 TRIS buffer. The premixed sample was allowed to stand for 2-3 min, and then an aliquot was injected directly into the fluorimeter flow cell for analysis. The flow cell was rinsed out thoroughly with TRIS buffer between injections. Extensive washings of the sample lines in contact with catalase solution was required before reuse. This system was equivalent in sensitivity, precition and reability (albeit not in ease of operation!) to the system shown in Figure 3.

Calibrations and Quality Assurance Activities. Flow meters were calibrated versus a wet test meter. The ozone generator was cross-calibrated with a Dasibi Model 1003 UV absorbance ozone monitor. Hydrogen peroxide solutions used to generate H_2O_2 (g) were standardized by titration with $KMnO_4$ which had been standardized with gravimetrically prepared oxalate solutions. The NO reagent gas in air was obtained by dilution of a certified source (208 ppm NO in N_2, Scott Environmental) and was used without calibration checks. The POHPAA fluorescence technique was calibrated with prepared H_2O_2 (aq) standards as described above.

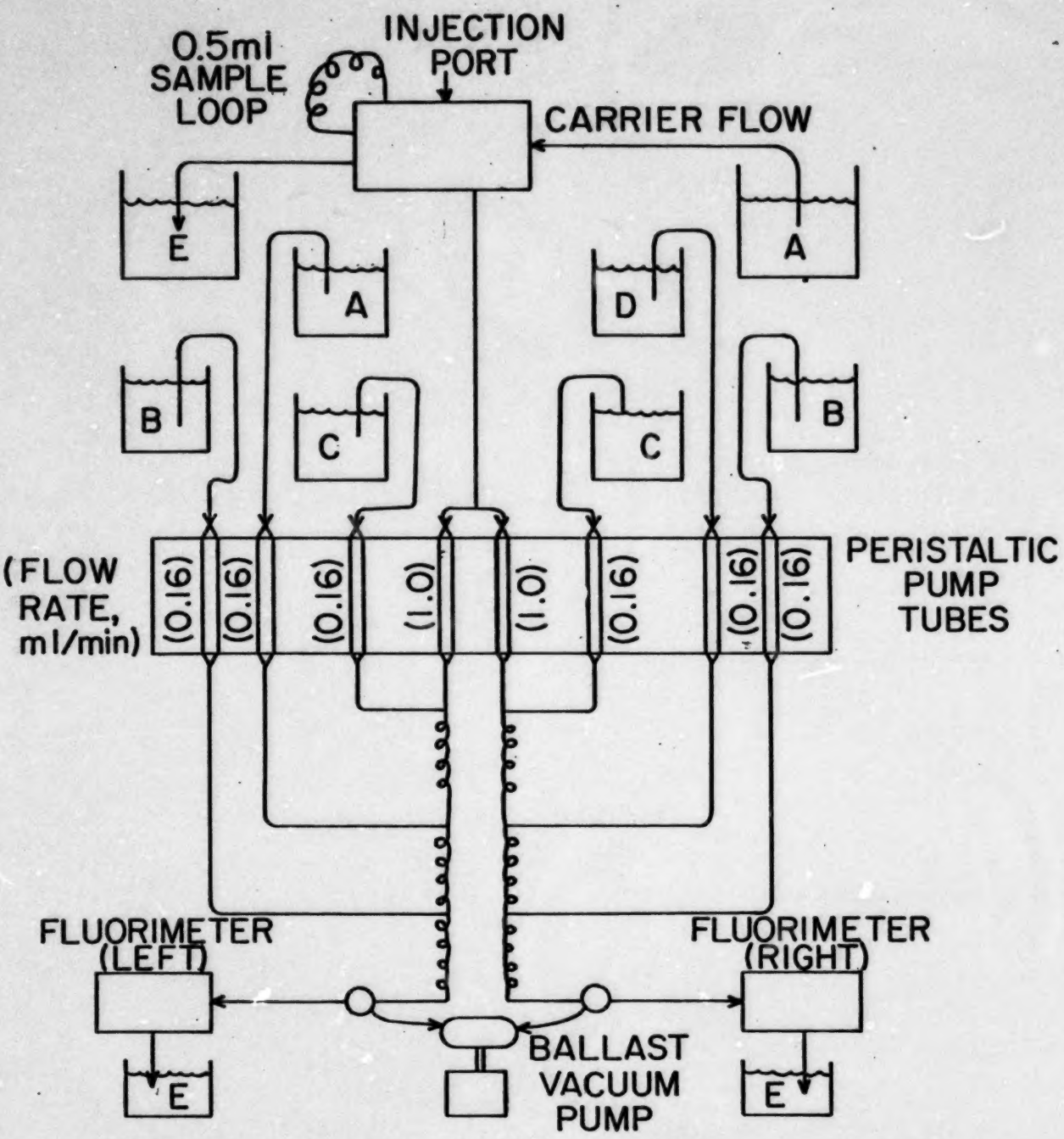

FIGURE 3

FLOW SCHEMATIC OF POHPAA FLUORESCENCE ANALYSIS SYSTEM FOR H_2O_2

RESULTS AND DISCUSSION

Aqueous Determination of H_2O_2. Considerable effort was expended to improve the POHPAA fluorescence technique for aqueous phase peroxide; additional effort was required by the fact that lower levels of peroxide would have to be analyzed for passive denuder-collected H_2O_2 samples or for artifact-free impinger collections (if such could be achieved). For example, data from Kelly et al. (1984) indicate that median peroxide levels from over 200 atmospheric water samples vary from ~5 μM for rain samples to ~8 μM for non-precipitating cloudwater samples, with intermediate levels in precipitating cloud samples. A peroxide level of 1 μM corresponds to ~33 ppb aqueous, hence most atmospheric water samples contain H_2O_2 at levels well above the LOD of even the original Farrand R2 dual channel system (LOD ~3 ppb 0.1 μM; Kelly, et al., 1984). However, ambient levels of gasecus H_2O_2 are predicted to be in the 0.1 to 1.0 ppbv range. Collection of H_2O_2 quantitatively into a midget impinger volume of 25 mL at 1 L/min for 1 hr results in concentrations of 0.3 to 3 ppb aqueous.

As a result of the above considerations, considerable effort was made to identify the causes of background noise in the POHPAA fluorescence technique. The progress in that regard was discussed in the Experimental Section above, with the note here included only to indicate that without improved analytical sensitivity, the stated goals of this task (0.1 ppbv, 15 min time resolution) would not be possible. Use of alternate chemistries involving reactive sampling of H_2O_2 onto coated denuder tubes do not negate these considerations since the fluorescence technique is at least as sensitive as readily substituted approaches (absorption spectroscopy or electrochemical methods), and radical improvements in the gas flow/liquid analytical volume are not practical using denuder sampling.

The final LOD achieved during this study of 0.3 ppb aqueous (~0.01 μM) appears just barely adequate to attain the task goal for the artifact-suppression or denuder approaches.

Denuder Tube Sampling

Pyrex denuder tubes, 0.6 cm OD by 30 cm long, were coated with ferrous-(1,10-phenanthroline)-sulfate solution in methanol as described above. They were then placed in the parallel air streams downstream from the mixing chamber and the Y and, in the case of line 2, after the addition of NO in N_2 to the air stream. Various admixtures of compressed air and ozone and/or H_2O_2 were passed through the denuders. Nitric oxide (6.2 ppm after dilution) was added to line 2 and the apparent H_2O_2 in each of impingers 2-1 through -3 and 1-1 through -3 was determined using the POHPAA fluorescence technique. The results of a complete set of these experiments are shown in Table 1.

After the initial experiment impinger 1-1 levels of H_2O_2(aq) increased irregularly from below the limit of detection (~0.01 μM) to as much as 0.34 μM. Essentially no H_2O_2 was found in impingers 2-2 and 2-3 when O_3 was removed (column 7) but significant levels were found in impingers 1-2 and 1-3 after experiment 3 whenever O_3 was passed through the denuder. When H_2O_2 only was added to either train of impingers, no H_2O_2 was found in either impinger 2 or 3 (experiments 8, 9 and 12). Artifact peroxide was also found for O_3- air mixtures using blank denuder tubes but not when O_3 was titrated by excess NO. The relatively even split of H_2O_2 in air sampled by sampling trains 1 and 2 is demonstrated by experiments 8 and 12.

The inferences to be drawn from this set of experimental data are as follows:

Table 1. Depletion of Ferroin-Coated Denuders

Experiment No.	H_2O_2 (μM) in Sampled Gas Stream 1			H_2O_2 (μM) in Sampled Gas Stream 2		
	Composition	Bubbler 1	Ave, Bubbler 2+3	Composition	Bubbler 1	Ave, Bubbler 2+3
1	O_3/H_2O_2/Air	0.031	ND[+]	O_3/H_2O_2/NO/Air	0.033	ND
2	"	ND	ND	"	ND	ND
3	"	0.029	ND	"	ND	ND
4	"	0.15	0.053	"	0.064	ND
5	"	0.34	0.068	"	0.068	ND
6	"	0.26	0.030	"	0.062	ND
7	"	0.10	0.081	"	0.11	ND
8	H_2O_2/Air	0.080	ND	H_2O_2/Air	0.074	ND
9	"	0.063	<0.01	"	0.10	0.013(?)
10	O_3/Air	0.19	0.10	O_3/NO/Air	0.02	<0.01
11	"	0.16	0.097	"	0.032	0.016
12*	H_2O_2/Air	0.41	ND	H_2O_2/Air	0.36	ND
13*	O_3/Air	0.14	0.081	O_3/Air	0.16	0.061
14*	O_3/Air	0.071	0.011	O_3/NO/Air	ND	ND

[+]ND = none detected

*Blank denuders used

Gas-Phase Conditions:

[Ozone] = 350 ppb ± 10%

$[H_2O_2]$ ≃ 20-25 ppb (determined from results of Expt. No. 12)

[NO] = 6.2 ppm

Sampling Conditions

Air sampled for 20 min at 0.5 L/min in each line.

(1) Ferroin-coated denuder tubes of the type tested have limited capacity for H_2O_2 removal, but they also remove O_3 at continuously decreasing efficiency.

(2) Ferroin-coated denuders do not prevent artifact H_2O_2 formation in impingers downstream of the denuder.

(3) Based on the experiences of Heikes (1984), ozone reacting on the denuder surface may generate artifact H_2O_2 on partially exhausted denuder tubes. This could explain experiments 10 and 11 in which small amounts of peroxide were formed and collected in impingers 2-1, 2-2 and 2-3 even in denuded air in which added O_3 had been titrated by NO. No mixing chamber was present between the NO addition point and the denuder, and unreacted O_3 could have produced small amounts of H_2O_2 and precursors on the denuder walls.

The original goal, after testing the efficiency and capacity of the ferroin denuder, ~~was to~~ develop a spectroscopic technique for the ferric product of ferrous complex oxidation by H_2O_2. After the above experiments were performed and it became obvious that ozone-denuder coating reactions were occuring in partially exhausted denuder tubes, probably generating H_2O_2 or its radical precursors, no further attempts were made to develop an absorption spectroscopic technique for determining traces of ferric(1,10-phenanthroline) [or substituted phenanthroline] complexes in the presence of excess ferrous complex as determined in wash solutions from the denuder tubes. We do not wish to assert that all iron(II) complexes would exibit the same behavior when used as denuder coatings as did ferroin, but only that the denuder approach as defined was heretofore unsuccessful in removing H_2O_2 quantitatively. In addition, complications are introduced due to

co-removal of ozone and presumably co-reaction with the ferroin (iron II-phenanthroline comples), possibly with accompanying generation and collection of artifact H_2O_2. Thicker coatings would increase the capacity of the tubes to acceptable levels and presumably do so without introducing microscale turbulence affecting the assumption of negligibly low particle collection efficiency. However, it would still be necessary to remove ozone in the gas stream prior to sampling in order to use ferrous-complex denuder coatings as proposed, hence negating the potential advantages of the denuder approach vis-a-vis impinger collection.

Gas-to-Liquid Sampling After O_3 Removal

As noted above, previous observations have suggested that artifact H_2O_2 formed in gas-to-liquid sampling using impingers or other approaches seems to be related to levels of ozone and one or more other air constituents (Heikes, 1984; ten Brink et al., 1983). As a result, sampling approaches in which ozone is selectively removed from the sampled air may be successful in eliminating the artifact formation of H_2O_2 while simultaneously transmitting H_2O_2 at high, reproducible efficiency to an aqueous solution for POHPAA analysis of H_2O_2. Evidence does suggest that the amount of H_2O_2 formed in bubbers is non-linearly related to O_3 concentration in sampled air (ten Brink et al, 1983; Groblicki, 1983) but since O_3 reaction on the bubbler surfaces appears to be the initial and limiting step in artifact H_2O_2 formation (Heikes, 1984), pre-removal of O_3 prior to sampling should effectively eliminate the process.

The evidence that titration with excess NO removes artifact H_2O_2 formation in impinger collection of H_2O_2 is shown in Table 2. Hydrogen peroxide (calculated to be 28 ± 2 ppb in stream 1, 22 ± 4 ppb in stream 2 from

Table 2. Collection of H_2O_2 from Ozone-Containing and Ozone-Free Air Streams

Experiment No.	H_2O_2 (μM) in Sampled Gas Stream 1			H_2O_2 (μM) in Sampled Gas Stream 2		
	Composition	Bubbler 1	Ave, Bubbler 2+3	Composition	Bubbler 1	Ave, Bubbler 2+3
1	H_2O_2/Air	0.58	ND*	H_2O_2/Air	0.56	ND
2	"	0.55	"	"	0.39	ND
3	O_3/Air	0.36	0.022	O_3/Air	0.31	0.014
4	O_3/H_2O_2/Air	0.96	0.018	O_3/H_2O_2/NO/Air	0.52	ND
5	"	0.63	0.016	"	0.45	ND
6	O_3/Air	0.15	ND	O_3/NO/Air	0.026	ND
7	"	0.044	ND	"	ND	ND
8	"	0.047	ND	"	ND	ND
9	O_3/H_2O_2/Air	0.69	0.060	O_3/H_2O_2/NO/Air	0.50	ND

*ND = none detected (<Blank)

Gas Phase Concentrations:
[Ozone] = 327 ± 13 ppb (Expts. 3-9)
[H_2O_2] = 28.0 ± 2.0 ppb (Stream 1); 22.2 ± 3.6 ppb (Stream 2)
[NO] = 6.2 ppm

Sampling Conditions:
Air sampled for 30 min 0.50 L/min in each line.

liquid-phase analyses) was admitted without O_3 or NO in Expts. 1 and 2; peroxide was found in roughly equal amounts in bubblers 1-1 and 2-1 (bubbler 2 = 101±34% of bubbler 1, for mean peroxide levels ≅ 6x limit of detection) No peroxide was found in subsequent bubblers. Ozone at 327 ± 13 ppb was admitted to the system in Expts. 3 through 9, with NO (6.2 ppm) present in stream 2 only for Expts. 4 through 9. In Expt. 3, addition of ozone alone to both streams produced H_2O_2 in all impingers with most (~90%) being found in impinger 1 of each stream. Addition of ozone + H_2O_2 mixtures to stream 1 and O_3/H_2O_2/NO to stream 2 (Expts. 4, 5 and 9) produced additional peroxide concentrations in all stream 1 bubblers consistent with the results of Expt. 3, but no peroxide was formed in stream 2 bubblers sampling NO-containing air (no H_2O_2 in bubblers 2-2 and 2-3, same amount of H_2O_2 in bubbler 2-1 as the average of experiments 1 and 2).

The amount of artifact H_2O_2 sampled from O_3-containing air streams is variable, and appears to be reduced in Expts. 5 to 9 compared with Expts. 1 to 4. Indeed, no artifact H_2O_2 was formed in impingers 2-2 and 2-3 during Expts. 6 to 8. In contrast, only in Expt. 6 was a small amount of H_2O_2 found in the O_3/NO/Air stream. This could be due to inadequate mixing of NO with the ozone/air stream, but is more likely the result of desorption of H_2O_2 retained in the mixing chamber from the previous experiment. Nevertheless the preponderance of evidence suggests that, even with a mixing delay of only about two 1/e-halflives after NO addition, ozone is removed sufficiently enough that no measurable artifact H_2O_2 is formed in subsequent sampling with a midget impinger.

Artifact H_2O_2 is formed in variable amounts when sampling the air stream containing about ~300 ppb O_3; collected amounts correspond to about 3-15 ppb of gaseous H_2O_2 in the first bubbler and roughly an order of magnitude lower in subsequent bubblers. This differs somewhat from earlier results (Heikes et al., 1982) in which roughly equal amounts of peroxide were formed in subsequent bubblers - indeed it is different from our own early results, suggesting that the extent of the process in which artifact H_2O_2 is formed is quite dependent on the presence of other atmospheric constituents in addition to O_3. The identity of these constituents is unknown, although certain possibilities have been excluded by the work reported in Volume II of this report. That these constituents may differ widely in their aqueous solubility is suggested by the low production rate of artifact H_2O_2 in impingers 2 and 3 compared to impinger 1 for the experiments summarized in Table 2.

One additional experiment should be described. Bubbling of ~6 ppm NO through water with subsequent analysis for H_2O_2 sometimes resulted in negative peaks, that is, fluorescence readings less than zero on the calibration curves for POHPAA analysis. It has not been demonstrated that this effect is, in fact, due to an interference from NO, since H_2O_2 concentrations are read from least-squares fits of calibration data and a small negative curvature in the actual readings is apparent at low H_2O_2 levels (< ~3 ppb). In addition, small negative peaks have been observed in ambient liquid water samples. The low aqueous solubility of NO makes direct interference with POHPAA analysis unlikely in the absence of aqueous reaction.

SUMMARY AND CONCLUSIONS

The research approaches investigated experimentally in this task for artifact-free sampling of $H_2O_2(g)$ included:

1. selective, reactive sampling onto a coated denuder tube, employing H_2O_2 redox chemistry;

2. suppression of *in situ* H_2O_2 formation by selective removal of ozone.

A denuder approach was attempted employing Fe(II)-1,10-phenanthroline-coated glass tubes. Hydrogen peroxide was removed by such tubes but collection efficiencies less than calculated values were observed even with relatively fresh tubes. This suggested that surface depletion of sorption sites was reducing the capacity of *dry* coating on the diffusion tube. In addition, ozone was removed to a significant extent by the Fe(II)-phenanthroline denuber tubes, indicating a lack of specificity for H_2O_2 and raising the spectre of surface decomposition of O_3, possibly to gas phase HO_2 and/or H_2O_2. Thus, removal of H_2O_2 onto denuders by nominally H_2O_2-specific chemisorption does not appear to offer significant advantages over gas-to-liquid sampling for gaseous H_2O_2 analysis.

Suppression of *in situ* production of H_2O_2 in gas-to-liquid sampling (bubblers, impingers) by upstream titration of the ozone content of the sampled air stream (approach 2) has been successfully demonstrated for cases in which compressed air is used. Gaseous hydrogen peroxide was collected completely (>99%) in the first bubbler whereas confluent ozone produced measurable peroxides in the 2nd and 3rd bubblers in series; no peroxide was observed in 2nd and 3rd bubblers for those experiments in which O_3

(100-300 ppb) was titrated by ~6 ppm NO prior to bubbler collection. The addition of 6 ppm NO does not significantly interfere with POHPAA analysis of collected H_2O_2(aq).

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